

Superior Performance of a Nanostructured Platinum Catalyst in Water: Hydrogenations of Alkenes, Aldehydes and Nitroaromatics

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Abstract: The hydrogenations of $>C=C<$, $>C=O$ and nitro groups in $ArNO_2$, with a water-soluble, polymer [poly(diallyldimethylammonium chloride)] supported, platinum carbonyl cluster $\{[Pt_{30}(CO)_{60}]^{2-}\}$ derived catalyst **1**, have been studied. The performance of **1** has been compared with that of two other platinum catalysts: catalyst **2** prepared by the hydrogen reduction of $[PtCl_6]^{2-}$ supported on the same water-soluble polymer, and **3**, a commercial platinum catalyst (5% Pt on alumina). Our catalyst **1** has been found to be more active than **2** and **3**, and by TEM it has been shown that the nanoparticles in **1** are much smaller than those in **2**. In the hydrogenation of *o*-chloronitrobenzene both **1** and **2** were found to be more selective (no hydrodehalogenation) than **3**. To evaluate the advantages of water as

a solvent, comparative studies have been carried out in three different solvent systems: water, methanol and a 1:1 mixture of water and toluene. Hydrogenations in methanol have been found to be accompanied by induction times while no such induction time is observed in water. Both liquid (methyl pyruvate, benzaldehyde, safflower oil and styrene) and water-insoluble solid nitroaromatics (*o*- and *m*-chloronitrobenzene and *p*-aminonitrobenzene) have been tested as substrates, and for all the substrates the activity in water was found to be higher.

Keywords: hydrogenation catalysts; ionic polyelectrolyte; nanocatalyst; on-water effect; platinum carbonyl cluster

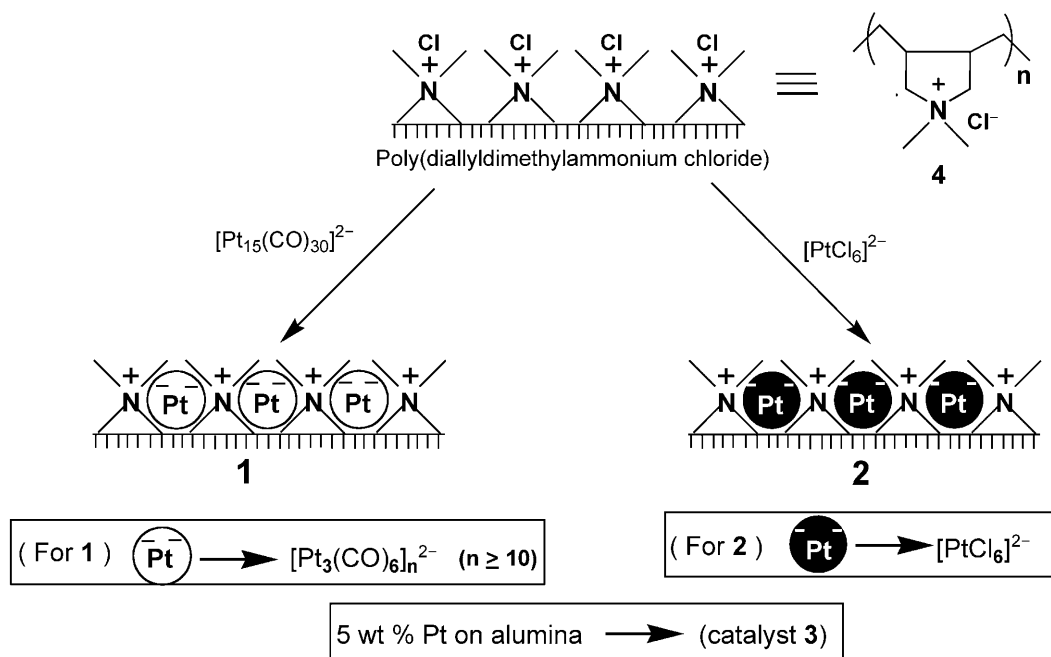
Introduction

From the point of view of environmentally benign chemical processes, the use of water rather than organic solvents is an important theme of current research.^[1–5] In industrial processes if the catalyst is water-soluble, but the products are immiscible or insoluble, the separation of products from catalyst can be easily achieved.^[6] Also many organic reactions when carried out in water have been reported to yield improvements in rates and selectivities.^[7–12] Especially noteworthy is the report where insoluble reactants stirred in aqueous suspensions, a condition designated as “*on-water*”, show rate acceleration.^[13–14] There is also a recent report where the selectivity of a gold nanocatalyst has been found to be critically dependent on the solvents employed.^[15]

Very recently we have shown^[16] that catalyst **1** could be prepared by supporting the platinum carbon-

yl cluster $[Pt_{30}(CO)_{60}]^{2-}$, on a water-soluble polymer, poly(diallyldimethylammonium chloride), **4** (Scheme 1). The freshly prepared polymer supported material has CO-protected platinum nanoparticles within the size range of 2–8 nm with *ca.* 40% being within 4–6 nm. This material catalyzes the selective hydrogenation of double bonds of $>C=C<$ and $>C=O$ functionalities in water. During catalysis the CO ligands are lost but the basic nanometric features of the platinum particles are retained. The above-mentioned reports^[1–15] on the remarkable influence of water and other solvents on rate and selectivity, prompted us to investigate the performance of the cluster-derived catalyst in greater detail.

The work presented here was undertaken with the following three primary objectives. First, scrutinizing the activity and structural differences, if any, between the cluster-derived catalyst **1** and that of another literature reported^[17] platinum nanocatalyst, **2**



Scheme 1. Designations of the support and different catalysts used in this work.

(Scheme 1). This comparison is important since the preparation of **2** involves hydrogen reduction of $[\text{PtCl}_6]^{2-}$ in the presence of **4**, i.e., the polymer used by us for the synthesis of **1**. Second, it is important to compare the performance of these two nanocatalysts with that of a commercial platinum catalyst (5% platinum on alumina) **3**, so that the advantages of nanocatalysts could be conclusively established. Third, we needed to see whether water is indeed the best medium for the cluster-derived catalyst from the point of view of rates and/or turnover numbers (TON). Moreover, we wanted to find out if with our catalyst, the “*on-water*” effect, i.e., increased rates with sparingly water-soluble solid substrates, could also be achieved. As described below, our results have revealed that **1** and water are indeed the best catalyst and reaction medium, respectively.

Results and Discussion

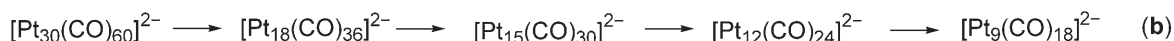
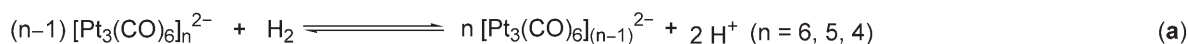
Performance of **1** for the Hydrogenation of Methyl Pyruvate and Nitrobenzene in Water and Methanol

The synthesis and characterization of the poly(diallyldimethylammonium chloride)-supported, high nuclearity Chini cluster $[\text{Pt}_{30}(\text{CO})_{60}]^{2-}$ by spectroscopy (IR, NIR, NMR) and TEM has recently been reported by us.^[16] The freshly prepared, polymer-supported material has CO-protected platinum nanoparticles within the size range of 2–8 nm with *ca.* 40% being within 4–6 nm. The particles of different sizes result from loose aggregations of the parent cluster, i.e., forma-

tion of clusters of clusters. Our compound **1** catalyzes selective hydrogenations of double bonds of olefinic ($>\text{C}=\text{C}<$) and carbonylic ($>\text{C}=\text{O}<$) functionalities, but under hydrogen pressure, i.e., catalytic conditions, loses the CO groups and there is a general decrease in the size of the nanoparticles. The time-monitored spectrophotometric changes of **1** on reaction with dihydrogen have been shown to be consistent with the known reactions (a) and (b) of Scheme 2.^[16] The overall reduction in the size of the nanoparticles under hydrogenation conditions is most probably due to the formation of aggregates of lower nuclearity, decarbonylated clusters (see later).

As the main objective of the work presented here was to evaluate the advantages of using **1** as a catalyst and water as a solvent, we first studied the hydrogenation of methyl pyruvate and nitrobenzene. The reasons for choosing methyl pyruvate were to see if in the presence of *Cinchona* alkaloids, **1** could catalyze the enantioselective formation of methyl lactate. Enantioselective hydrogenation of methyl pyruvate using heterogeneous platinum catalysts and *Cinchona* alkaloids as chiral modifiers is a much studied reaction.^[18–20] Enantioselective hydrogenations of pyruvate esters have also been reported for colloidal platinum-based, *Cinchona* alkaloid-modified catalytic systems.^[21,22]

Surprisingly, either in water or in methanol, using **1** as the catalyst and *Cinchona* alkaloids as chiral modifiers, no enantioselectivity could be obtained in the hydrogenation of methyl pyruvate. This is in contrast to the behaviour of a cinchonidium-functionalized mesoporous silica (MCM-41)-supported, platinum



Scheme 2. Reduction of a platinum carbonyl cluster (Chini cluster) in the presence of dihydrogen.

cluster-derived catalyst.^[20] The obvious conclusions from these results are that the catalytic properties of **1** are different from those of cinchonidium-functionalized MCM-41 catalysts. More importantly, although both $[\text{PtCl}_6]^{2-}$ -derived colloidal platinum and **1** can be used as nanocatalysts in water, they show important difference in terms of selectivity. Most probably in the case of **1**, the polymer matrix prevents the easy coordination of cinchonidine to the platinum particles, thereby ruling out the formation of enantioselective sites.

With **1** as the catalyst, good turnovers (1200) of methyl pyruvate to methyl lactate are obtained over a period of *ca.* 12 h in water. In methanol more time (*ca.* 16 h) is required for the same extent of reaction and, as can be seen from Figure 1, there is a remarkable difference between the initial rates in these two solvents. In methanol there is an induction time when the catalyst shows less activity, but in water there is no such induction time. Thus in methanol and water the initial turnover frequencies (TOF) measured over three hours are 28 and 160 h^{-1} , respectively.

Similar differences in the initial rates are also observed in the hydrogenation of nitrobenzene in methanol and water. Nitrobenzene was chosen because we wanted to explore the scope of the hydrogenation reaction beyond that of $>\text{C}=\text{C}<$ or $>\text{C}=\text{O}<$ double

bonds. We also wanted to study the selectivity of hydrogenation of *o*-chloronitrobenzene, and the “on-water” effect with solid nitroaromatics (see later). As shown in Figure 1 (inset), **1** catalyzes the hydrogenation of nitrobenzene to aniline, with *ca.* 1200 turnovers in 60 and 80 min in water and methanol, respectively. Here again in methanol there is an induction time and the initial TOF measured over 20 minutes are 24 and 2.4 min^{-1} respectively.

In all our previous works where platinum carbonyls had been used as the precursor of supported catalysts we have established that the platinum clusters lose the CO ligands before or during catalysis.^[16,20] We had also shown that the polystyrene-supported clusters become catalytically active only after thermal or photochemical decarbonylation, i.e., when they are coordinatively unsaturated.^[23] The existence of an induction time in methanol and its absence in water are therefore due to the fact the carbonyl ligands are lost rapidly in water, but less rapidly in methanol.

Comparative Performances of 1–3 for the Hydrogenation of Double Bonds in $>\text{C}=\text{C}<$ and $>\text{C}=\text{O}<$ Functionalities

The comparative catalytic activities of **1**, **2** and **3** in water have been evaluated for the hydrogenation of a few representative substrates that have $>\text{C}=\text{C}<$ or $>\text{C}=\text{O}<$ double bonds (see Table 1). The hydrogenation of safflower oil, the triglyceride of mainly (~80%) linoleic acid (*cis,cis*-9,12-octadecadienoic acid, see Figure 2, inset), is a reaction of considerable industrial importance. On its hydrogenation in water the oil layer turns into a waxy solid. The extent of hydrogenation can be conveniently measured by ¹³C NMR by monitoring of the intensities of the signals due to the olefinic carbons. As can be seen from Figure 2, when **1** is used as the catalyst, only a negligible amount of residual unsaturation remains in the product.

As can be seen from Table 1, for the hydrogenation of safflower oil, **2** and **3** give very similar but notably fewer turnovers than **1**. The change in the iodine value, a traditional way of measuring relative unsaturation in oils and fats, also indicates that **1** is more active than **2** and **3** (see Experimental Section). Thus the initial iodine value of 115 of safflower oil drops to 22, 47 and 48, for **1**, **2** and **3**, respectively. It is also

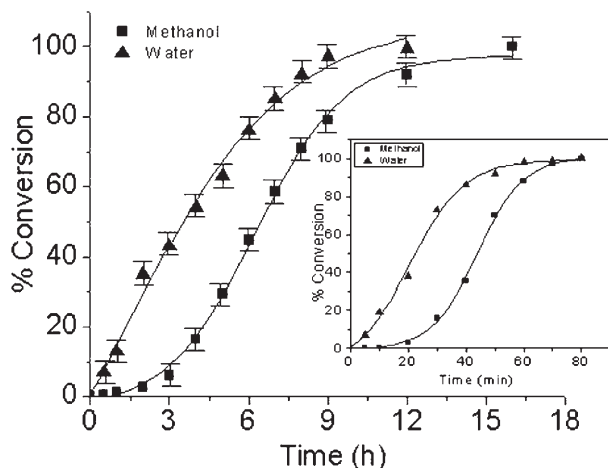
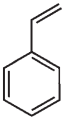
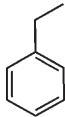
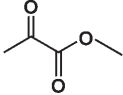
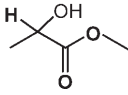


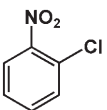
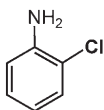


Figure 1. Comparative time-monitored conversion plot in water and methanol for methyl pyruvate and nitrobenzene (inset) hydrogenation catalyzed by **1**. Reaction conditions: 300 K, 50 bar hydrogen pressure, 10 mL solvent (water or methanol), substrate to catalyst molar ratio 1200:1.

Table 1. Comparative catalytic activities of **1**, **2** and **3**.^[a]

Entry No.	Substrate	Product	Substrate amount/Time [h]	Catalyst	% Conversion (TON)
1	Safflower Oil	Hydrogenated Safflower Oil ^[b]	2 g/24 h	1	>98% (142)
2				2	81 (115)
3				3	80 (114)
4			1 g (9.6 mmol)/12 h	1	100 (1180)
5				2	98 (1156)
6				3	97 (1144)
7			1 g (9.8 mmol)/12 h	1	100 (1202)
8				2	80 (961)
9				3	83 (997)
10			1 g (10.6 mmol)/6 h	1	99 (1145)
11				2	50 (578)
12				3	45 (520)
13			2 g (15.7 mmol)/2 h	1	100 (1558)
14				2	90 (1402)
15				3	55 (857)

^[a] Hydrogenation of typical substrates catalyzed by **1–3** in water. *Reaction conditions*: catalyst amount equivalent to 8.15×10^{-3} mmol of platinum, 50 bar H₂ pressure, solvent (water) 5 mL, temperature 300 K (except for safflower oil 353 K). Products were analyzed by GC and ¹H NMR.

^[b] TON calculated on the basis of molecular weight of the triglyceride of linoleic acid.

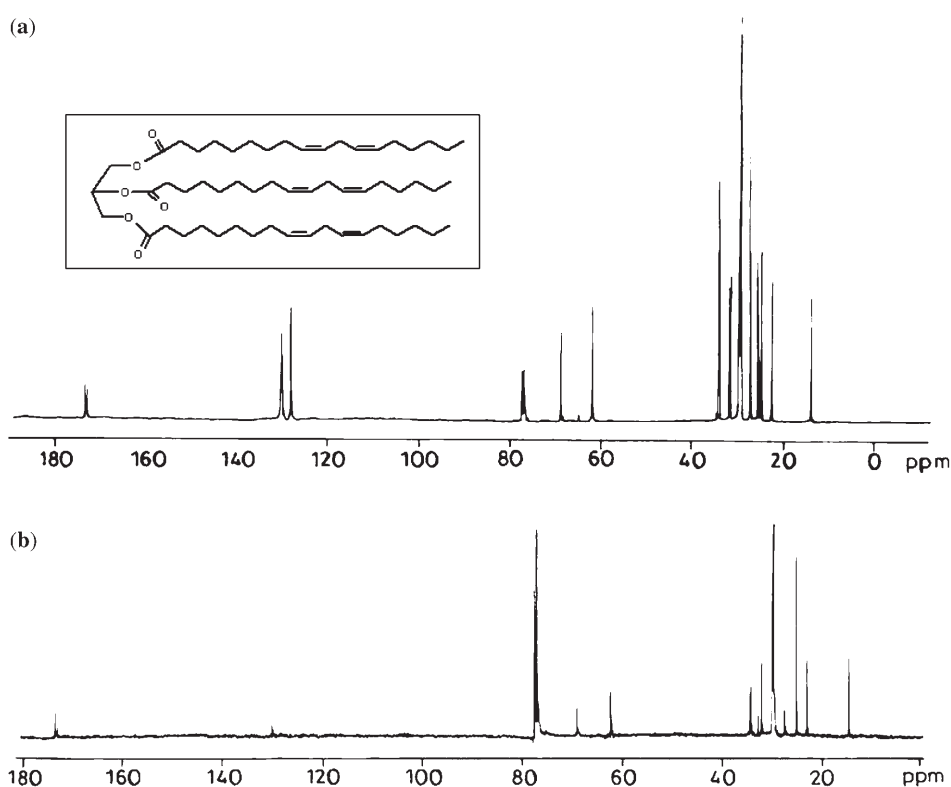

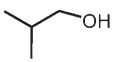
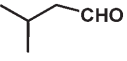
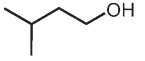
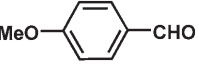
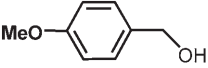
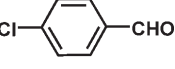
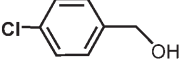


Figure 2. (a) ¹³C NMR spectrum (¹H decoupled) of safflower oil and (inset) the structure of the main constituent of safflower oil: triglyceride of linoleic (*cis,cis*-9,12-octadecadienoic) acid. (b) ¹³C NMR spectrum (¹H decoupled) of hydrogenated safflower oil.

Table 2. Comparative catalytic activities of **1**, **2** and **3** in the hydrogenation of aldehydes.^[a]

Entry no.	Substrate	Product	Substrate amount/Time [h]	Catalyst	% Conversion (TON)
1			1 g (13.88 mmol)/6 h	1	99 (1686)
2		2		88 (1498)	
3		3		52 (885)	
4			1 g (11.49 mmol)/6 h	1	98 (1381)
5		2		80 (1127)	
6		3		35 (493)	
7			1 g (7.35 mmol)/6 h	1	73 (658)
8		2		32 (288)	
9		3		39 (351)	
10			1 g (7.11 mmol)/6 h	1	99 (863)
11		2		52 (453)	
12		3		75 (654)	

^[a] Hydrogenation of typical aldehydes apart from benzaldehyde catalyzed by **1–3** in water. *Reaction conditions:* catalyst amount equivalent to 8.15×10^{-3} mmol of platinum, 50 bar H₂ pressure, solvent (water) 5 mL, temperature 300 K. Products were analyzed by GC and ¹H NMR.

clear from the conversion data of styrene, methyl pyruvate, benzaldehyde and *o*-chloronitrobenzene that for all of these substrates **1** is more active than **2** or **3**. In most of the cases significantly higher turnovers are obtained with **1** and the activities of the three catalysts are approximately in the order of **1** > **2** ≈ **3** except for *o*-chloronitrobenzene where the order is **1** > **2** > **3**.

Among these test substrates, for the hydrogenation of benzaldehyde to benzyl alcohol, **1** is about twice as active as the other two. In view of these findings, the relative activities of **1–3** have been evaluated for two aliphatic and two other aromatic aldehydes and the results are given in Table 2. Catalyst **1** is found to be clearly more active than both **2** and **3** for all the aldehydic substrates.

In metal-catalyzed reactions, the correlation between smaller particle size and higher catalytic activity is a well established observation.^[24] TEM micrographs of **1** and **2** have been recorded to see if the difference in their relative activities could be due to such a difference in particle size. As shown in Figure 3, the platinum particles in **2** are indeed much larger (>20 times) than the ones in **1**, and while in **1** the particle size ranges from 2 to 8 nm, in **2** it ranges from 40 to 200 nm. Thus the TEM data clearly show that for smaller nanoparticles, platinum carbonyls rather than hexachloroplatinate must be used.

There are many reports on catalysis with cluster-derived materials.^[25,26] It may be noted that the general trend for the cluster-derived nanoparticles to grow after a *large numbers* of catalytic turnovers is *also* observed for **1**. In nitrobenzene hydrogenation, after turnovers ≥ 2500, platinum particles of ~10 nm sizes are seen at the boundaries of the polymer support (see Supporting Information). The general reduction in the sizes of the nanoparticles reported by us earlier^[16] refers to micrographs recorded after ~500–1000 turnovers. As mentioned earlier this is due to the formation of aggregates of *lower nuclearity, decarbonylated cluster of clusters*. This explanation is strongly supported by control experiments (catalytic run without substrates) where similar reductions in size are consistently observed.

It may also be noted that the reactions shown in Table 1 are chemoselective, there is no hydrogenation

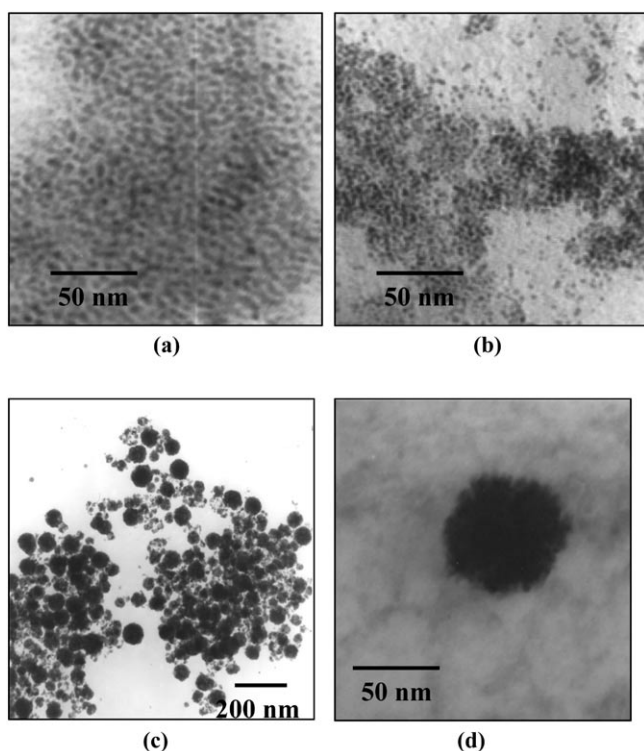


Figure 3. (a), (b) TEM images of freshly prepared and used **1**. (c), (d) TEM images of used **2** at two different magnifications.

of the aromatic rings or the ester group, neither is there any hydrogenolysis of benzyl alcohol. The selectivity aspect is of special relevance for the hydrogenation of *o*-chloronitrobenzene. The chemoselective reduction of *o*-chloronitrobenzene with the avoidance of the hydrodehalogenation product aniline is of considerable industrial importance.^[27–29] In so far as platinum catalysts are concerned, it has been shown that high selectivity could be achieved only *in supercritical* carbon dioxide.^[28] A recent report also shows that nanoparticles of cobalt and Ni-Pd are very effective for the hydrogenation of a variety of nitroaromatics.^[29] Another recent report describes gold nanoparticle-catalyzed, selective reductions of nitro groups in the presence of other functional groups.^[30] In view of these reports, the products from the hydrogenations of *o*-chloronitrobenzene with **1–3** as catalysts have been carefully analyzed.

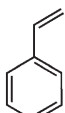
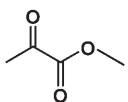
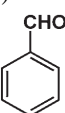
With **1** as the catalyst, the hydrogenation of *o*-chloronitrobenzene in an aqueous suspension yields only *o*-chloroaniline. No aniline or any other by-product is detected by high-sensitivity gas chromatography (detection limit $\geq 0.4\%$). However, under identical conditions **3** gives $\sim 2\%$ aniline. Interestingly, the other nanocatalyst **2** also does not give detectable levels of aniline. Finally, it may be noted that although *o*-chloronitrobenzene is a solid and practically insoluble in water, its efficient hydrogenation can be carried out in an aqueous suspension. This aspect has been further studied and is discussed in the following section.

Superiority of Water as a Solvent

As mentioned in the Introduction, one of the central themes of this work was to evaluate whether or not with **1** as the catalyst, water as a reaction medium offers any special advantage. This question has been addressed by carrying out hydrogenations of both liquid and solid substrates. The liquid substrates chosen for this purpose are immiscible in water, while the solids, all nitroaromatics, are sparingly soluble in water. For the liquid substrates comparative studies have been carried out in water, methanol and a biphasic medium consisting of a 1:1 (by volume) mixture of water and toluene. The superiority of water over both mixed solvent and methanol is evident from the ratios of the TON obtained in different media (Table 3). Thus, for styrene, methyl pyruvate and benzaldehyde, the ratios of the TON in water, a mixture of water and toluene, and in methanol are: 100:18:72; 100:79:69; and 100:63:99.

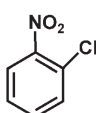
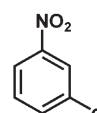
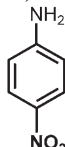
As mentioned earlier, higher TON and rates for water-insoluble solids have recently been reported for a Diels–Alder reaction and this phenomenon has been described as “*on-water*” effect.^[13,14] In view of this we wanted to find out if for the solid nitroaromat-

Table 3. Effect of solvent on TON for liquid substrates.^[a]

Solvents	% Conversion (TON)		
			
Water	100 (1180)	100 (1202)	99 (1145)
Water-toluene	18.2 (215)	79 (950)	62 (717)
Methanol	72.7 (858)	69 (834)	97.9 (1133)

^[a] Hydrogenation of water immiscible liquid substrates catalyzed by **1** in three different media. Reaction conditions: metal content 8.15×10^{-3} mmol, substrate 1 g, 50 bar H₂ pressure, reaction time 12 h (for benzaldehyde 6 h), solvent 5 mL, temperature 300 K.

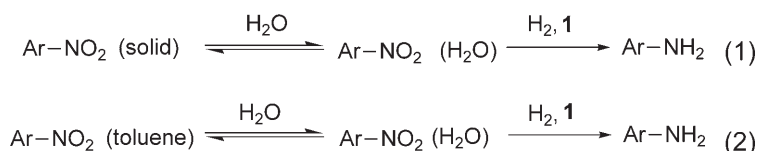
Table 4. Effect of solvent on TON for solid nitroaromatics.^[a]

Solvents	% Conversion (TON)		
			
Water	100 (1558)	75 (1168)	100 (1778)
Water-toluene (1:1)	80 (1250)	40 (623)	66 (1173)

^[a] Hydrogenation of three substrates catalyzed by **2** in two different media. Reaction conditions: metal content 8.15×10^{-3} mmol, Substrate 2 g, 50 bar H₂ pressure, reaction time 120 min, solvent 5 mL, temperature 300 K. Products were analyzed by GC and ¹H NMR. Solid substrates were first grinded to fine powdery form and then added to the aqueous catalyst solution. In water-toluene biphasic system, substrates were dissolved in toluene.

ics, which are practically insoluble in water, any special advantage in terms of TON might be observed. The catalytic hydrogenation reactions have been carried out in two different media: water and a biphasic medium consisting of water and toluene (1:1). As can be seen from Table 4, in water significantly higher turnover numbers (~ 25 – 50% more) are obtained for the hydrogenation of all the substrates. One of the factors for the enhanced rate may plausibly involve the equilibrium steps of Eq. (1) and Eq. (2) that schematically represent the reactions in the two media.

If the equilibrium step of Eq. (1) is thermodynamically more favorable than that of Eq. (2), then the relative concentrations of the nitroaromatics in the aqueous phase will also be more for Eq. (1). This would result in a higher rate for the catalytic hydrogenation step that follows.



Conclusions

In conclusion, ion pairing of a platinum carbonyl cluster with the quaternary ammonium groups of a water-soluble polymer gives a platinum nanocatalyst that is more active than a nanocatalyst prepared by hydrogen reduction of $[\text{PtCl}_6]^{2-}$, or a commercial platinum catalyst. Between the two nanocatalysts (**1** and **2**), the cluster gives much smaller nanoparticles than $[\text{PtCl}_6]^{2-}$. In the hydrogenation of *o*-chloronitrobenzene both the nanocatalysts show higher chemoselectivity than the commercial platinum catalyst. For representative substrates including safflower oil and insoluble organic solids, the activities in water are found to be greater than those in methanol or a 1:1 mixture of water and toluene.

Experimental Section

Preparation of the cluster-derived catalyst and subsequent manipulation with it were performed using standard Schlenk techniques under an atmosphere of nitrogen. Solvents were dried by standard procedures (methanol over Mg-turnings/iodine), distilled under nitrogen, and used immediately. Starch solution was prepared according to conventional procedure prior to the titration for iodine value determination. All hydrogenation reactions were performed in an autoclave at 300 K. $^1\text{H}/^{13}\text{C}$ NMR spectra were recorded on a 400 MHz Varian spectrometer. TEM experiments were performed using a Philips 1200 EX at 120 kV. UV-vis-NIR measurements were performed on a Perkin Elmer lambda-950 spectrophotometer. FT-IR spectra were taken on a Nicolet spectrophotometer with samples prepared as KBr pellets. All the samples were analyzed by gas chromatographic techniques with an FID detector (Shimadzu GC-14 A gas chromatograph) using a capillary column (CBP20M-25-025). The bulk platinum content of fresh catalyst **2** was determined on an 8440 Plasma Lab ICP-AES instrument.

Poly(diallyldimethylammonium chloride) (polyDADMAC, low molecular weight), 20 wt% solution in water, sodium hexachloroplatinate, methyl pyruvate, acrylic acid, styrene, 5% platinum on alumina were purchased from Aldrich, Germany and used as received. Carbon monoxide was supplied by BOC, India. Resublimated iodine, mercurous chloride, carbon tetrachloride, sodium acetate, benzaldehyde and all aromatic nitro compounds were purchased from SD fine chemicals, India and used after proper distillation. Safflower oil was taken from a local market. All other chemicals were of reagent grade and used after proper distillation prior to the catalytic experiments. Distilled water was used for the catalytic studies in water or biphasic water

medium. Catalysts **1** and **2** were prepared and characterized by the methods reported in our earlier work.^[16] Catalyst **3** was purchased from Aldrich Germany and used as received.

Experimental Catalytic Conditions

All hydrogenation reactions were carried out in an autoclave under hydrogen pressure at 300 K. In a typical experiment 150 mg of catalyst were dissolved in either 5 mL distilled water or methanol in a 20-mL beaker and 1 g of substrate was added to it. Then it was kept under the specified hydrogen pressure in the autoclave at 300 K (otherwise mentioned in special cases) for the respective time with vigorous stirring. After the reaction the product was separated by solvent extraction with ethyl acetate and subsequently analyzed by GC or proton NMR spectroscopic techniques. Biphasic reactions were carried out in 1:1 (v/v) water and toluene/ethyl acetate by following a similar method.

The TON of safflower oil hydrogenation was determined from the ^1H NMR spectrum of hydrogenated safflower oil. Due to hydrogenation the peak area for olefinic hydrogens (at 5.3 ppm) decreases considerably but that of the glycerol moiety (at 4.2 ppm) remains unaffected. By comparing the peak areas of these two signals, remaining olefinic unsaturation is calculated. Iodine values of safflower oil and its hydrogenated product were estimated using the Hübl method which is a standard technique for the determination of iodine value.^[31]

Supporting Information

TEM picture of used catalyst (after 2500 TON) with nitrobenzene as a substrate (Figure S1).

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